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Analysis of Nitroglycerine in Soils and on Mortar Fins Using GC-TID

Alan D. Hewitt

February 2002

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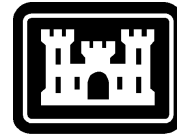
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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Environmental Sciences Branch, U.S. Army Cold Regions Research and Engineering Laboratory, Engineer Research and Development Center. Funding for this work was provided by the U.S. Army Environmental Center, Martin H. Stutz, Project Monitor. Technical reviews were provided by Thomas F. Jenkins and Marianne Walsh, both of CRREL.

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Analysis of Nitroglycerine in Soils and on Mortar Fins Using GC-TID

ALAN D. HEWITT

1 INTRODUCTION

There is growing awareness that military training and testing activities involving high explosives and propellants release residues of energetic materials to the local environment (Jenkins et al. 1997, Thiboutot et al. 1998). Recently the U.S. Environmental Protection Agency halted future training and testing exercises at the Massachusetts Military Reservation (MMR) following the discovery of low levels of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in the groundwater beneath an impact range (U.S. EPA 2000a). This action served notice to the U.S. Armed Forces that they must become better environmental stewards of their training ranges. To address this concern, several programs have been initiated to characterize residues of explosives and propellants on impact ranges and firing points. These efforts have already established that RDX; 2,4,6-trinitrotoluene (TNT); 2,4-dinitrotoluene (2,4-DNT); octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); and nitroglycerine (NG) can persist on training ranges (USACHPPM 2000, USEPA 2000a, Ogden Environmental and Energy Services 2000, Jenkins et al. 2001, Walsh et al. 2001). However, the source strengths, fate, and transport mechanisms for explosives and propellant residues that are released to the environment as a result of training and testing activities remain under investigation.

NG (glycerol trinitrate, $C_3H_5N_3O_9$) is manufactured for use in dynamites, military explosives (e.g., ignition cartridges), and multi-based propellants and has pharmaceutical applications (Urbanski 1965). NG is a high explosive that is sensitive to shock, impact, and friction and is usually desensitized with other materials when used in commercial and military explosives (Yinon 1999). NG is toxic to humans and can enter the body through dermal absorption, inhalation, or ingestion. Exposure to NG often results in a reduction in blood pressure and under some circumstances can be fatal (Yinon 1990).

The ability to quickly characterize the spatial distribution of NG and other targeted explosive or propellant residues in soil is difficult at most military training facilities because of their vast sizes (tens of thousands of acres) and remoteness. A confounding factor for active training or testing ranges is that they are continuously being altered physically and chemically. Because of these factors it is prudent to use on-site analysis and dynamic sampling plans for characterization. Currently there are two sets of on-site analytical methods—4050 and 4051; 8510 and 8515—recognized by the U.S. Environmental Protection Agency (U.S. EPA) for the determination of explosives (U.S. EPA 1996a, b, c, 2000b). These two sets of methods are well suited for the detection of TNT and RDX. Moreover, methods 8510 and 8515 can also be used to detect other nitroaromatics, nitramines, nitrate esters, or groups of these compounds, such as nitroaromatics vs. nitramines and nitrate esters (Crockett et al. 1998). However, neither of the method sets is selective enough to simultaneously identify multiple nitroaromatic, nitramine, and nitrate ester explosives.

As a consequence we have been evaluating a field-portable gas chromatograph (GC) equipped with a thermionic ionization detector (TID). This detector is selective for compounds containing nitro (NO_2) functional groups and certain other electronegative compounds (Patterson 1986). Coupling this detection system with chromatographic separation establishes the capability to identify and measure all of the explosives and propellants previously targeted, as well as several others. Hewitt et al. (2001) demonstrated that concentration estimates for TNT, RDX, 2,4-dinitrotoluene (2,4-DNT), and other explosives established by GC-TID analysis were very consistent with high-performance liquid chromatography (HPLC) and GC-electron capture detection (GC-ECD) (U.S. EPA Methods 8330 and 8095, respectively) (U.S. EPA 1994, 1999).

The principal focus of this study is to present an evaluation of NG determination by GC-TID analysis. In addition, a sampling protocol that was used to locate elevated levels of another common propellant (2,4-DNT) near 105-mm howitzer firing positions is briefly discussed.

2 MATERIALS AND METHODS

The GC used was a Model 8610C manufactured by SRI Instruments (Torrance, CA) equipped with a heated (250°C) TID detector, a heated (225°C) on-column injection port, and an internal air compressor. This instrument currently sells for less than \$9K and requires a personal computer (\$1K) for controlling oven temperature programs and for collecting and handling data. This GC is very transportable and can be set up for operation in about 30 minutes. Separations were performed on a glass Crossbond 100% dimethyl polysiloxane column (DB-1), 15-m \times 0.53-mm i.d., 0.5- μ m film thickness (Restek, Rtx-1). Injections of 1 μ L of acetone were made manually with a 10- μ L glass syringe (SGE). The carrier gas was high-purity nitrogen flowing at 37 mL/min, and the TID potential was set at -3.40 V. In addition, air was supplied to the detector from the onboard compressor at a rate of approximately 15 mL/min. The oven temperature program was to hold at 95°C for 0.5 min, then ramp at 40°C/min to 220°C, ramp at 20°C/min to 240°C, and hold for 0.375 min. The program resulted in baseline resolution for NG, 2,4-DNT, TNT, RDX, and HMX (Hewitt et al. 2001). Sample injections were made about every 6 min.

Calibration Standards

An NG analytical stock standard (5.00 mg/mL) was purchased from AccuStandard, Inc. (New Haven, CT). A mixed stock standard (each analyte at 1.00 mg/mL) containing the 14 explosives-related analytes listed in Method 8330 was purchased from the same source. Both of these stock standards were specially prepared using acetone as the solvent. The techniques for preparing and handling the mixed analyte working standards can be found elsewhere (Hewitt and Jenkins 1999).

Sample Preparation

To screen the surfaces of mortar fins (an item frequently identified as range scrap on impact ranges) for NG and other explosives and propellant residues, the surface was rubbed with a small cotton ball (approximately 2.5 cm in diameter) moistened with 1 mL of acetone (Hewitt 2001). The ball was held with metal tweezers and was air-dried after wiping. Once dry, the cotton ball was pressed into the barrel of a 5-mL disposable plastic syringe and a 25-mm Millex FH (0.45- μ m) filter attached via a Luer-Lok™ fitting. Following the addition of 1 mL of acetone to the cotton ball in the syringe, the plunger was inserted into the barrel to compress the cotton ball and force excess solvent through the filter and into a 2-mL amber deactivated glass vial.

Soil samples were prepared by extracting 2.0–10 g of soil with an equal to two-fold greater volume of acetone (i.e., 1:1 to 1:2). Extractions were performed in glass bottles for at least 30 minutes. To facilitate extraction the sample was dispersed by intermittently shaking the bottle for 15-second intervals. This extraction protocol has been shown to be quantitatively accurate for recovering explosives from several types of soils (Jenkins et al. 1997). Following extraction, an aliquot of the acetone was passed through a 25-mm Millex FH (0.45- μ m) filter that was attached, via a Luer-Lok™ fitting, to a disposable 3-mL plastic syringe. The filtered extract was directly transferred to a 2-mL amber deactivated glass vial.

Instrument Calibration

To calibrate the GC-TID instrument, five working standards were prepared. The concentrations of the working standards typically ranged from 0.25 to 20 μ g/L for NG and from 0.125 to 10 μ g/L for many of the other explosives and propellants. Calibration checks were made after every five samples by randomly running one of working standards. When the calibration model failed to establish a concentration within 20% of the expected value for an analyte of concern, the instrument was recalibrated.

3 EXPERIMENTS

Both laboratory and field studies were performed to assess GC-TID analysis of NG. Laboratory studies included a Method Detection Limit (MDL) evaluation (Federal Register 1984), an analysis of archived soil samples, and an analysis of residues recovered from the surface of mortar fins. The field study consisted of an on-site analysis of soil samples at Ft. Greely, Delta Junction, Alaska, as part of a training range characterization program. Likewise, all of the soil samples and mortar fins analyzed for NG were collected during sampling events that were assessing explosives residues on active military training ranges.

The MDL study was performed using 5.0 g of Ottawa sand spiked at 0.50 mg/kg for NG, 0.10 mg/kg for HMX, 0.05 mg/kg for RDX, and 0.010 mg/kg for 2,4-DNT and TNT. The acetone-based spike solution was injected onto Ottawa sand contained in a glass vial. After the soil was allowed to air-dry for 1 hr, it was extracted with 5.0 mL of acetone. The results of this study are in Table 1.

Two to six subsamples were taken from laboratory-archived soils that had previously been determined to contain NG. One of the samples was collected in an impact crater, and three others were collected at firing points. These archived samples had been air-dried, sieved (2 mm), and thoroughly mixed. Table 2 shows the GC-TID and GC-ECD results for the analysis of these subsample extracts.

Table 1. GC-TID method detection limit (MDL) results for NG, 2,4-DNT, TNT, RDX, and HMX on Ottawa sand spiked at 0.50, 0.010, 0.010, 0.050, and 0.10 mg/kg, respectively.					
Replicate no.	NG (mg/kg)	2,4-DNT (mg/kg)	TNT (mg/kg)	RDX (mg/kg)	HMX (mg/kg)
1	0.61	0.013	0.011	0.055	0.087
2	0.52	0.014	0.011	0.055	0.087
3	0.60	0.014	0.011	0.050	0.10
4	0.59	0.013	0.011	0.055	0.10
5	0.58	0.013	0.010	0.060	0.086
6	0.61	0.012	0.010	0.054	0.11
7	0.62	0.013	0.011	0.057	0.099
Mean	0.59	0.013	0.011	0.055	0.095
Std Dev.	0.337	0.00069	0.00049	0.0030	0.0096
MDL	0.10	0.0021	0.0015	0.0091	0.029

Two sets of mortar fins were sampled. These mortar fins were collected at two different impact ranges and were from rounds that had NG as an ingredient either in a multi-based propellant or in the ignition cartridge. For the first set, two 120-mm mortar fins that were recovered from impact craters immediately after firing (detonation) were sampled. Both of these fins were covered with soot and had been deformed. Four areas (each approximately 30 cm²) were wiped on each fin: the inside and outside walls of the stem, the bottom inside the stem, and between one set of the tail guides. The second set consisted of ten 60-mm mortar fins from illumination rounds. They were recovered from a seasonally flooded salt marsh used as a military impact range. Three of the mortar fins were identified by an explosives ordnance expert as having been fired during the previous winter's training exercises, while the remaining rounds had been on the range for years. The age of the mortar fins was determined by the appearance of oxidation on the aluminum and steel surfaces. When sampling the surface of these ten illumination rounds, we wiped between two sets of the tail guides (approximately 65 cm²). Table 3 contains the NG results obtained for both sets of fins determined by GC-TID, GC-ECD, and HPLC analysis.

Table 2. Comparison between GC-TID and GC-ECD (Method 8095) for NG in archived soil sample extracts.

Sample ID	NG (mg/kg)	
	GC-TID	Method 8095
A1	<0.1	0.033
A2	<0.1	0.018
B1	5.0	6.1
B2	29	43
B3	27	35
B4	11	11
B5	2.6	2.4
B6	10	8.8
C1	0.16	0.46
C2	0.42	0.79
D1	<0.1	0.029
D2	<0.1	0.015

Table 3. GC-TID, GC-ECD, and HPLC (Methods 8095 and 8330) results for NG in extracts of surface wipe samples of mortar fins.				
a. 120-mm mortar fins (30 cm² wiped)				
	NG (ng/cm²)			
	Fin A		Fin B	
	GC-TID	Method 8095	GC-TID	Method 8095
Stem exterior	9.7	8.7	330	370
Stem interior	77	67	120	83
Between tail guides	4.0	6.3	240	140
Bottom interior	40	31	67	57
b. 60 mm mortar fins (65 cm² wiped)				
	NG (ng/cm²)			
	GC-TID	Method 8330		
1 – old	98	95		
2 – old	860	860		
3 – old	120	91		
4 – old	320	320		
5 – old	680	650		
6 – old	290	230		
7 – old	150	110		
8 – new	1700	1400		
9 – new	1200	1100		
10 – new	1800	2000		

At Ft. Greely the GC-TID system was used to analyze for NG and other explosives and propellant residues in surface soil samples. The majority of samples were collected as composites from within specified grids. Most of the sampling grids were positioned where it was evident that munitions had been exploded or fired (Walsh et al. 2001). Each composite sample was composed of approximately 1 kg of material obtained by collecting soil and vegetation from 30 or more randomly chosen locations. In addition to the composite samples, some large discrete samples were collected within craters or near munitions fragments. Clean metal spoons were used to transfer the soil (surface material) to clean polyethylene bags for transportation and storage. Clean spoons were also

used to obtain subsamples of 7 ± 4 g for on-site GC-TID analysis. Subsamples were taken from the bulk samples by combining small amounts from at least ten random locations into a 20-mL glass bottle. Both the bulk samples and subsequent subsamples were moist and frequently contained pebbles, grasses, weeds, and mosses. In a few cases animal droppings (moose and American bison) were also collected as part of these composite samples. Subsamples were extracted with 10–15 mL of hardware-store-grade acetone and were analyzed at a rate of 35 ± 10 samples per day.

The main objective for using on-site GC-TID analysis was to identify locations with elevated concentrations of NG and other explosives and propellant residues. Ft. Greely was chosen as a site for this study because NG had been found at a firing position for 40-mm cartridges (rifle grenades) that was sampled during the reconnaissance visit. The propellant used in the 40-mm rounds was 77.2% nitrocellulose and 19.4% NG. Unfortunately we were unable to obtain clearance from range control to revisit this particular impact range and were unable to locate another 40-mm cartridge firing position. On-site GC-TID analysis did, however, establish the presence of other explosives and propellant residues in about half of the 90 samples collected around howitzer firing positions. The most frequently detected target analyte was 2,4-DNT, followed by TNT. In addition, there were several samples from the firing positions that appeared (based on a retention time match) to contain pentaerythritol tetranitrate (PETN). Only one of these samples from the howitzer firing positions was determined to contain NG. Similarly, of the 49 samples taken from impact ranges, only one was determined to contain NG. In general, much fewer hits were established for explosives and propellants in the impact range samples. As with the firing positions, 2,4-DNT was the most frequently detected explosive.

One of two samples determined to contain NG was composed mostly of sand that was collected as a discrete sample on an impact range next to a mortar fin. The other was a composite composed of soil, grass, weeds, and moss that had been collected at a howitzer firing point. To increase the number of NG analyses performed during this field study, we resampled both of these bulk samples. Five and ten additional replicate 5.0-g subsamples were removed from the sample taken next to the mortar round and the firing point sample, respectively. Prior to the collection of these additional replicates, the bulk samples had been placed in aluminum pie plates and had started to air-dry. As with the original subsamples that were removed from these bulk samples, all of these additional subsamples were composed of small amounts from 10 or more locations. Following on-site analysis the sample extracts were packed in a cooler and returned to the Cold Regions Research and Engineering Laboratory (CRREL) for further analysis.

The results obtained for these subsample extracts on-site by GC-TID and at CRREL by GC-ECD and HPLC appear in Table 4.

Table 4. Comparison between on-site GC-TID and laboratory GC-ECD and HPLC (Methods 8095 and 8330) results for NG in soil sample extracts prepared at Ft. Greely.			
Sample ID	NG (mg/kg)		
	GC-ECD	GC-TID	HPLC
GI-003	5.1	4.7	6.5
GI-003-S1	16	25	23
GI-003-S2	19	27	23
GI-003-S3	4.8	11	10
GI-003-S4	<0.03*	<0.1	<1 [†]
GI-003-S5	<0.03	<0.1	<1
Sally-23	32	32	33
Sally-23-S1	<0.03	<0.1	<1
Sally-23-S2	<0.03	<0.1	<1
Sally-23-S3	<0.03	<0.1	<1
Sally-23-S4	<0.03	<0.1	<1
Sally-23-S5	0.81	0.65	<1
Sally-23-S6	1.1	0.93	<1
Sally-23-S7	<0.03	<0.1	<1
Sally-23-S8	<0.03	<0.1	<1
Sally-23-S9	<0.03	<0.1	<1
Sally-23-S10	6.7	5.0	5.7
* Method detection limit (Walsh and Ranney 1999).			
[†] Estimated method detection limit for HPLC-UV (254 nm).			

4 RESULTS AND DISCUSSION

The detection limit evaluation established an MDL of 0.10 mg/kg for NG by GC-TID analysis (Table 1). MDLs for 2,4-DNT, TNT, RDX, and HMX are also included in this table because these explosives have been detected frequently on military training ranges (Walsh et al. 2001). The analysis of archived soils and mortar fin wipes showed that there was very good agreement among NG values established by GC-TID, GC-ECD, and HPLC (Tables 2 and 3). Figure 1 is a linear regression of the GC-TID and HPLC results from Table 3. This data set was selected for the regression analysis because HPLC is more precise than GC-ECD. The regression analysis resulted in a correlation coefficient greater than 0.96 and a slope (1.02) that was very close to the theoretical value of 1.00.

In Table 2, samples B through D were obtained in July 2000 during a reconnaissance visit to Ft. Greely. These three samples had been collected near a 40-mm cartridge firing position. The large variation (e.g., a range of 2.4–43 mg NG/kg for sample B) in NG concentrations obtained for the subsample replicates shows that this analyte was not distributed homogeneously after air-drying, sieving (2 mm), and mixing the bulk sample.

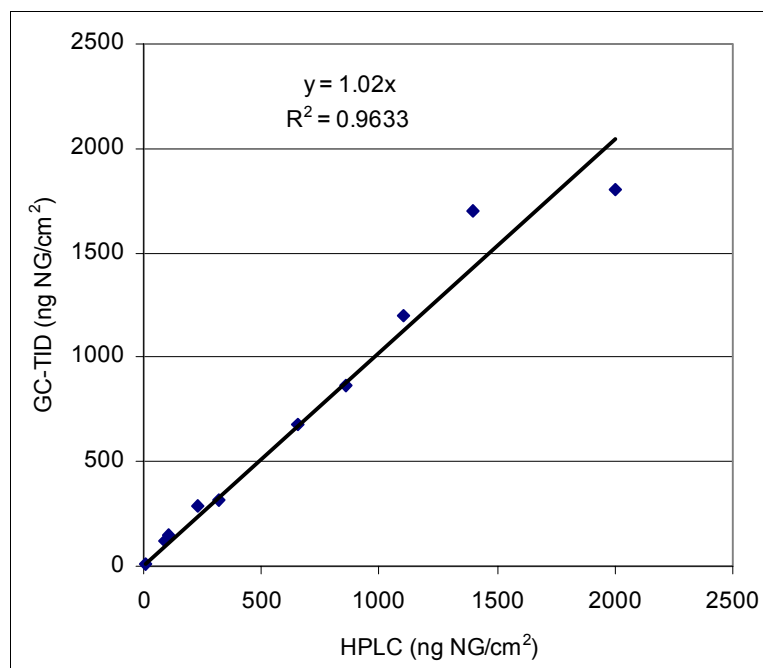


Figure 1. Correlation analysis of GC-TID surface wipe concentration samples compared to those from HPLC-UV analysis for splits of sample extracts.

This level of variation among subsample replicates has been observed for several other explosives (Walsh and Ramsey, in prep.). Walsh and Ramsey (in prep.) studied the effects of both subsample size and particle size reduction. Subsamples ranged from 2 to 50 g. Particle sizes were reduced manually using a mortar and pestle to break up aggregates followed by passage through 10 and 30 mesh sieves (i.e., Method 8330) and by using a ring and puck mill to grind the material to a fine powder (ground material capable of passing through a 200 mesh sieve^{*}). The results of their study showed that it was necessary to mechanically grind the bulk sample to a fine powder before representative subsampling could be accomplished on a routine basis. One explanation for this finding is that explosives residues associated with detonations are randomly dispersed as particles that are very different in size or shape, or both, from the soil they fall upon. Conventional laboratory mortar and pestle grinding (Method 8330) does not effectively change the shape and size of individual particles, only particle clusters.^{*} When samples are composed of particles that have a variety of sizes or shapes, or both, subsampling is very susceptible to segregation error.

The wipe samples taken from various locations on the 120-mm mortar fins that were collected immediately after being fired showed that NG residues were present on all of the surfaces wiped (Table 3a). The samples taken from the 60-mm mortar fins indicated that NG was not quickly removed or degraded, even when exposed to sunlight and moisture (Table 3b). Even the fins that appeared to have been exposed for a longer period prior to collection continued to show fairly high concentrations of NG on the surface. The moderate solubility and higher vapor pressure of NG would suggest that this compound should have a shorter environmental half-life than most other explosives and propellants (Table 5). The persistence of NG on mortar fins, which perhaps lasts for a decade or longer[†] indicates that other factors, such as surface adsorption, play a role.

On-site analysis of surface soil samples at Ft. Greely was performed for seven consecutive days. It rained periodically during the first three days of this field exercise, elevating the moisture content of the samples collected. The presence of water in the sample extracts caused a continuous slow loss in sensitivity for NG and the other analytes throughout the course of each day. However, with the exception of HMX, it was determined that analyte sensitivity could be returned to the pre-field trial conditions by removing approximately 150 cm from the front end of the column. The ability to detect HMX was lost after the

^{*} Personal communication, C. Ramsey, EnviroStat, Inc., P.O. Box 636, Fort Collins, CO 80522-0636.

[†] Personal communication, M. Walsh, CRREL.

Table 5. Physical properties of selected nitroaromatics and nitramines.					
Analyte	CAS reg. no.	Molecular weight	Melting point (°C)	Water solubility (mg/L)	Vapor pressure at 20°C (torr)
NG	55-63-0	227.09	13.2*	1500@20°C*	2.6E-04*
TNT	118-96-7	227.13	80.1-81.6 [†]	130@20°C [†]	1.1E-06 [†]
RDX	121-82-4	222.26	204.1 [†]	42@20°C [†]	4.1E-09 [†]
HMX	2691-41-0	296.16	276-280 [†]	5@20°C [†]	3.3E-14 [†]
2,4-DNT	121-14-2	182.15	70 [†]	270@22°C [†]	2.2E-04 [†]
* Yinon (1999)					
[†] Walsh et al. (1993)					

third day of operation. The slow loss of analyte sensitivity and the loss in the capability to detect HMX were the only instrument problems that were encountered. The first of these two problems was addressed by cutting approximately 150 cm off the front end of the column at the beginning of each day and by re-calibrating periodically. The capability to perform on-site HMX analysis most likely would be improved by drying the samples. All of the NG on-site GC-TID values reported in Table 4 were established on the last day of the field study by grouping all of the samples into a single run using the same calibration model.

Table 4 shows NG results established on-site by GC-TID and in the laboratory by GC-ECD and HPLC for the Ft. Greely soil sample extracts. This data set shows that there was good agreement between the different methods of analysis and highly variable NG concentrations among the subsample replicates. These results demonstrate that there was much greater uncertainty (error) associated with sampling than with the method of analysis. Indeed, several of the subsamples failed to show the presence of NG, while others were two and three orders of magnitude above the instrument's limits of detection. This wide range in concentrations was present in both sets of subsamples, so it is apparently not matrix dependent. That is, the bulk sample composed mostly of sand and the one composed of a mixture of soil, grass, weeds and moss showed the same range of variation among subsample replicates. Jenkins et al. (1997) demonstrated the merits of using composite as compared to discrete sampling when addressing the average concentration of explosives over a given area. In their study, vegetation and rocks were removed, and the soil was air-dried and then thoroughly mixed prior to subsampling and on-site analysis. The time necessary to perform these tasks, particularly drying, limits the ability to establish preliminary on-site

results. Indeed, because many of the bulk samples collected at Ft. Greely were collected while it was raining and contained a large amount of vegetation, air-drying would have taken several days. The approach used for this field experiment was to collect small amounts from more than ten locations in the bulk samples to build each subsample for on-site analysis. Future efforts should assess other homogenization techniques that are both rapid and compatible with field operations, in an attempt to make subsamples removed soon after sample collection more representative.

The ability to rapidly determine which sampling locations (grids) were contaminated with explosives and propellant residues allowed the sampling team to look for hot spots. During the Ft. Greely field study, 2,4-DNT was the most frequently detected analyte, followed by TNT, NG, and perhaps pentaerythritol tetranitrate (PETN). The presence of PETN, however, has yet to be confirmed by laboratory analysis. Because of the greater occurrence of 2,4-DNT, this analyte was targeted for further study. Two firing positions were chosen for looking for hot spots of this propellant residue. When sampling to locate surface hot spots, we collected ten discrete samples of approximately 10 g in size from a single grid at each firing point. These smaller discrete samples were extracted in entirety for on-site analysis. Following the analysis of these discrete samples, the locations within each of these two grids with the highest 2,4-DNT concentration were profiled. Shallow (first 15-cm) profile sampling was performed at these hot spots to assess the potential for vertical migration of this analyte. This strategy would also apply to studying the environmental fate and transport of NG on training ranges.

5 SUMMARY

The determination of NG by GC-TID analysis established results that were consistent with Methods 8095 and 8330. This agreement was demonstrated with laboratory and field soil samples and with wipe samples of mortar fins. Earlier research had shown that there is good agreement among these methods of analysis for several other explosives (2,4-DNT, TNT, and RDX) (Hewitt et al. 2001). Therefore, not only can GC-TID analysis be used to determine NG, but this method can be used for the analysis of several other explosives and propellants that are typically found on training ranges (Walsh et al. 2001). The ruggedness, selectivity, and quick turn-around time of analysis for GC-TID makes this analytical method very attractive for field programs that would benefit from dynamic sampling and analysis, for example, when studying the fate and transport of NG on military training ranges. This study also emphasized that caution must be exercised when interpreting results of subsamples removed from bulk samples that have not been air-dried, ground, sieved, and thoroughly mixed, because of the large potential for variability in the results.

LITERATURE CITED

Crockett, A.B., T.F. Jenkins, H.D. Craig, and W.E. Sisk (1998) Overview of on-site analytical methods for explosives in soil. Special Report 98-4, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. www.crrel.usace.army.mil/techpub

Federal Register (1984) Definition and procedure for the determination of the method detection limit. Code of Federal Regulations, Part 136, Appendix B, October 26.

Hewitt A.D. (2001) Characterization of range scrap and development of quality assurance coupons for hot gas treatment. ERDC/CRREL TR-01-7, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. www.crrel.usace.army.mil/techpub

Hewitt, A.D., and T.F. Jenkins (1999) On-site method for measuring nitroaromatic and nitramine explosives in soil and groundwater using GC-NPD: Feasibility study. Special Report 99-9, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. www.crrel.usace.army.mil/techpub

Hewitt A.D., T.F. Jenkins, and T.A. Ranney (2001) On-site gas chromatographic determination of explosives in soils. *Field Analytical Chemistry and Technology*, **5**(5): 228–238.

Jenkins, T.F., C.L. Grant, G.S. Brar, P.G. Thorne, T.A. Ranney, and P.W. Schumacher (1996) Assessment of sampling error associated with collection and analysis of soil samples at explosives-contaminated sites. Special Report 96-15, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. www.crrel.usace.army.mil/techpub

Jenkins, T.F., P.G. Thorne, M.E. Walsh, C.L. Grant, S. Thiboutot, G. Ampleman, T.A. Ranney, and M.H. Stutz (1997) Sampling strategy for site characterization at explosives-contaminated sites. *Proceedings of the Second Tri-service Environmental Technology Workshop, St. Louis, Missouri*.

Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren (2001) Characterization of explosives contamination at military firing ranges. ERDC TR-01-5, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. www.crrel.usace.army.mil/techpub

Ogden Environmental and Energy Services (2000) Evaluation of gun and mortar firing positions for the Camp Edwards Impact Area groundwater quality study, Massachusetts Military Reservation, Cape Cod, Massachusetts. Client

Draft IAGS Technical Team Memorandum 00-3, Ogden Environmental and Energy Services, Westford, MA 01886.

Patterson, P.L. (1986) Recent advances in thermionic ionization detection for gas chromatography. *Journal of Chromatographic Science*, **24**: 41–52.

Thiboutot, S., G. Ampleman, A. Gagnon, A. Marois, T.F. Jenkins, M.E. Walsh, P.G. Thorne, and T.A. Ranney (1998) Characterization of antitank firing ranges at CFB Valcartier, WATC Wainwright and CFAD Dudurn. DERV-R-9809, Defence Research Establishment, Valcartier, Quebec.

USACHPPM (2000) Training range site characterization and risk screening, Camp Shelby, Mississippi, 7-23 September 1999. Geohydrologic Study No. 38-EH-8879-99, Aberdeen Proving Ground, MD.

U.S. EPA (1994) Method 8330: Nitroaromatics and nitramines by HPLC. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-846 through Update 4b. www.epa.gov/sw-846.

U.S. EPA (1996a) Method 4050: TNT explosives in soil by immunoassay. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-846 through Update 4b. www.epa.gov/sw-846.

U.S. EPA (1996b) Method 4051: Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in soil by immunoassay. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-846 through Update 4b. www.epa.gov/sw-846.

U.S. EPA (1996c) Method 8515: Colorimetric screening method for trinitrotoluene (TNT) in soil. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-846 through Update 4b. www.epa.gov/sw-846.

U.S. EPA (1999) Method 8095: Nitroaromatics and nitramine by GC-ECD. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-846 through Update 4b. www.epa.gov/sw-846.

U.S. EPA (2000a) Administrative Order for Massachusetts Military Reservation Training Range and Impact Area Response Actions. EPA Docket No. SDWA-1-2000-0014. Region 1. Boston, MA.

U.S. EPA (2000b) Method 8510: Colorimetric screening procedure for RDX and HMX in soil. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-846 through Update 4b. www.epa.gov/sw-846.

Walsh, M.W., T.F. Jenkins, P.S. Schnitker, J.W. Elwell, and M.H. Stutz (1993) Evaluation of SW846 Method 8330 for characterization of sites contaminated with residues of high explosives. CRREL Report 93-5, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Walsh, M.W., and T.A. Ranney (1999) Determination of nitroaromatic, nitramine, and nitrate ester explosives in soils using GC-ECD. Special Report 99-12, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Walsh, M.W., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney (2001) Sampling for explosives-residues at Fort Greely, Alaska: Reconnaissance visit, July 2000. ERDC TR-01-15, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Walsh, M.W., and C. Ramsey (in prep) The effect of particle size reduction on subsampling variance for explosives residues in soil.

Urbanski, T. (1965) *Chemistry and Technology of Explosives*. Vol. II, New York: Pergamon Press.

Yinon, J. (1990) *Toxicity and Metabolism of Explosives*. Boca Raton, FL: CRC Press.

Yinon, J. (1999) *Forensic and Environmental Detection of Explosives*. New York: John Wiley and Sons.

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14. ABSTRACT A method of analysis for nitroglycerine (NG) in soil and on the surfaces of mortar fins (a common range scrap material) was developed using a field-portable gas chromatograph system. The method combines quick and simple sample preparation procedures with a rapid gas chromatographic (GC) analysis using a thermionic ionization detector (TID) that is selective for compounds containing nitro (NO ₂) functional groups. Very good agreement was observed among NG values established for splits of sample extracts by GC-TID and two accepted methods of analysis (high-performance liquid chromatography and GC electron capture). The method detection limit (MDL) for NG in soil established by GC-TID analysis was 0.1 mg/kg.					
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